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HARVARD COLLEGE.

*THE QUANTITATIVE DETERMINATION OF  
ANTIMONY BY THE GUTZEIT METHOD.*

BY CHARLES ROBERT SANGER AND EMILE RAYMOND RIEGEL.

WITH A PLATE.



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THE QUANTITATIVE DETERMINATION OF ANTIMONY BY  
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THE application of the so-called Gutzeit reactions to the quantitative determination of arsenic has been studied by Sanger and Black<sup>1</sup>, who were able to use the general method of Gutzeit<sup>2</sup> for the convenient and reasonably accurate estimation of small amounts of arsenic. In studying the interference of the hydrides of sulphur, phosphorus, and antimony with the reaction of arsine on paper sensitized with mercuric chloride, the possibility of the quantitative determination of antimony by this method was apparent.

The action of stibine on mercuric chloride was first investigated by Franceschi<sup>3</sup>, who obtained a white body, to which he gave the formula  $\text{SbHHg}_2\text{Cl}_2$ , analogous to the red compound formed by the action of arsine on mercuric chloride. This substance decomposes easily in moist air, turning dark, probably from the separation of mercury. When stibine is allowed to act upon sensitized mercuric chloride paper, as shown by Sanger and Black<sup>1</sup>, no color is given to the strip from amounts of antimonious oxide up to about 70 micromilligrams (mmg.). Hydrochloric acid develops no color. But if the strip is treated with ammonia, a black band ensues, the length and intensity of which are proportional to the amount of antimonious oxide present. On this reaction we have based the following method for the determination of small amounts of antimony.

<sup>1</sup> These Proceedings, **43**, 297 (1907); Jour. Soc. Chem. Ind., **26**, 1115 (1907); Zeitsch. f. anorg. Chem., **58**, 121 (1907); Suppl. ann. enciclop. chim., **24**, 372 (1907-08).

<sup>2</sup> Pharm. Zeitung, **24**, 263 (1879). In the original Gutzeit method, the evolved arsine was allowed to act upon paper containing argentic nitrate. From Flückiger in 1889 (Archiv d. Pharm., **227**, 1) came the suggestion of using mercuric chloride.

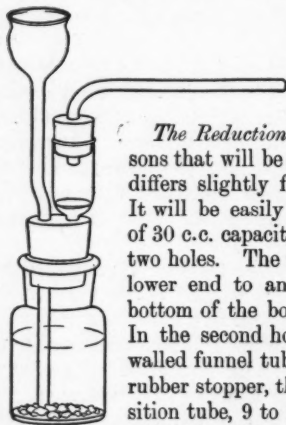
<sup>3</sup> L'Orosi, **13**, 397 (1890).

## THE METHOD.

The procedure does not vary greatly from that used in the determination of arsenic as described by Sanger and Black<sup>1</sup>. Some details, therefore, of that method are necessarily repeated here.

*Sensitized Mercuric Chloride Paper.* A smooth filter paper of close texture, or a Whatman drawing paper of about 160 grams per square meter, is cut into strips of a uniform width of 4 millimeters. The strips are sensitized by drawing them repeatedly through a five per cent solution of recrystallized mercuric chloride until thoroughly soaked. They are then dried on a horizontal rack of glass tubing, and,

when dry, are at once cut into lengths of six to seven centimeters. The small pieces are kept in the dark until needed, in a stoppered bottle over calcic chloride.



*The Reduction Apparatus.* (See Figure.) For reasons that will be explained later, the construction of this differs slightly from that used in the arsenic method. It will be easily seen from the figure. The bottle is of 30 c.c. capacity, closed by a pure rubber stopper with two holes. The thistle tube, which is constricted at its lower end to an opening of about 2 mm., passes to the bottom of the bottle and has a length of 17 to 18 cm. In the second hole of the stopper is inserted a straight-walled funnel tube of 17 to 20 mm. bore, carrying a pure rubber stopper, through which passes a right angle deposition tube, 9 to 10 cm. in length, the inner diameter of which should be as near 4 mm. as possible, but not less.

*Reagents.* These are exactly the same as in the arsenic method, and are entirely free from antimony. The zinc, Bertha spelter, is from the New Jersey Zinc Company of New York, and has been proved by repeated tests to be free from arsenic. The hydrochloric acid, from the Baker and Adamson Company of Easton, Pennsylvania, contains not over 0.02 milligram of arsenious oxide per liter. The quantity of diluted acid (one part to six of water) used in the analysis would not contain over 0.00004 milligram of arsenious oxide, an amount beyond the absolute delicacy of the method as applied to arsenic and hence of no influence in the determination of antimony.

*Moisture Conditions in the Deposition Tube.* As in the arsenic method, the moisture of the evolved hydrogen has an important bearing on the uniformity of the color bands. While excess of moisture must

be avoided in the arsenic method by a cotton wool filter, it is necessary to have a much greater degree of saturation in order to obtain compact and uniform deposits on the strips from stibine. If the hydrogen is partially dried by cotton wool before impinging upon the sensitized paper, the bands are long, irregular and not comparable. By increasing the saturation and by making it as uniform as possible we have succeeded in determining the conditions under which the bands are short, regular, and perfectly comparable.

To effect this and at the same time to hold back any hydrogen sulphide which might be formed in the reduction, we use disks of lead acetate paper inserted in the straight-walled funnel tube and moistened with a definite amount of water. These disks are of filter paper of medium thickness, cut in quantity by means of a wad cutter or cork borer so as to fit loosely the bore of the funnel tube. They are saturated with normal lead acetate, dried, and kept in a well stoppered bottle.

*Procedure.* The deposition tube and funnel tube of the apparatus are cleaned and thoroughly dried. A lead acetate disk is then inserted in the funnel tube and moistened with one drop of water, delivered on the centre of the disk, so that the water spreads evenly to the circumference. Three grams of uniformly granulated zinc are placed in the bottle, a strip of sensitized paper is slipped wholly within the deposition tube to a definite distance, and the apparatus is put together. Five or ten cubic centimeters of diluted acid (1 to 6; normality, about 1.5) are then added through the thistle tube and allowed to act for about ten minutes. The acid is then poured off and fifteen cubic centimeters of fresh acid added. This procedure ensures a uniform degree of moisture saturation in the deposition tube, and the absence of arsenic in the reagents and apparatus is assured. The zinc is also rendered more sensitive, and a regular flow of hydrogen is quickly obtained on the second addition of acid.

In five minutes after this addition, the solution to be tested is introduced, either wholly or in aliquot part, which may be determined by weighing or measuring. In case it were necessary from the nature of the analysis to prove the absolute freedom of the apparatus and reagents from arsenic and antimony before adding the solution, the evolution of hydrogen would be continued for a longer time and the strip developed. The absence of contamination being thus assured, a fresh strip would be substituted before adding the solution to be tested. In ordinary work, however, this precaution is quite unnecessary.

After the solution is introduced, the reduction is continued for 30 to 40 minutes. No effect on the sensitized paper is observed unless the amount of antimony added is above 70 mmg., when a slight gray

color may appear. Larger amounts would turn the paper still darker. If any color appears, it is an indication that the amount will be difficult to estimate, and hence another trial should be made with a smaller portion of the solution, or from less of the original substance.

The strip is now placed in a test tube and covered with normal ammoniac hydroxide, which is allowed to act for five minutes. A black band is slowly developed, somewhat duller and considerably shorter than would be obtained from the same amount of arsenic, the latter difference being chiefly due to the moisture conditions in the deposition tube. The band is then compared with a set of standard bands. The amount of antimony in the entire solution follows from that determined in the aliquot part.

*Standard Bands.* A standard solution is made from pure, recrystallized tartar emetic, shown to be free from arsenic. 2.3060 grams are dissolved in water and made up to one liter. This solution (I) contains 1.0 mg. of antimonious oxide per cubic centimeter. From this, by dilution, are made two solutions containing respectively 0.01 mg. (II) and 0.001 mg. (III) per cubic centimeter. From definite portions of solutions II or III a series of bands is made by the above procedure, using a fresh charge of zinc and acid for each portion. The lower half of the Plate shows the actual size and shading of the set of bands, corresponding to the following amounts of antimonious oxide in micromilligrams : 5, 10, 15, 20, 25, 30, 35, 40, 50, 60, 70.

These bands have shown a fair degree of permanency, but fade slowly on exposure to moisture and light. They may be sealed in glass tubes with quicklime, if desired, as in the case of the corresponding ammonia-developed arsenic bands, but we have found it sufficient to mount them on a dry glass plate, which is covered by a dry plate of the same size. The two plates are then cemented together and bound with passepartout paper. The set thus mounted, if kept in a desiccator away from the light, will last for some time. In case a fresh set of standards is not available, a band may be approximately estimated from the accompanying Plate; the more accurate determination being made, if necessary, by comparison with freshly prepared bands from selected amounts.

#### ANALYTICAL NOTES.

*General Precautions.* As in the arsenic method, the solution to be reduced should contain no interfering organic matter, except that any oxide of antimony obtained in the preparation for analysis may be eventually dissolved in tartaric acid. Sulphur in any form reducible to hydrogen sulphide should be removed as completely as possible, but

small quantities of hydrogen sulphide will be completely retained by the lead acetate disk. There is little danger from phosphine, for phosphites and hypophosphites would be oxidized in any treatment of the substance to be analyzed which would convert the antimony to the oxide. Traces of phosphine would be readily recognized in presence of antimony<sup>4</sup>, but are likely to interfere with its estimation. It is obvious that there must be a very thorough separation from arsenic.

*The Evolution of Stibine in the Reduction Bottle.* Sanger and Gibson<sup>5</sup> have shown that amounts of antimony under one milligram are practically all converted to hydride in the presence of zinc and hydrochloric acid, hence a retention of antimony by precipitation upon the zinc is not to be considered in the estimation of the small amounts provided for by this method.

*Special Precautions.* In order to be certain of uniformity in length and density of bands from the same concentration of solution, the following points must be observed:

1. The reduction bottles must be of equal capacity, and other parts of the apparatus of equal dimensions.
2. The amount of zinc must always be the same, similarly sensitized, and the granulation must be uniform.
3. The volume and concentration of the acid must be definite.
4. The moisture conditions in the deposition tube must be carefully regulated, as explained above.

In the "Analytical Notes" of the article by Sanger and Black<sup>1</sup>, many suggestions will be found which will contribute to a clearer understanding of this method as well, but which are not included here for the sake of brevity.

#### ANALYTICAL DATA.

The method, as far as it concerns the determination of antimony in a solution properly prepared for reduction, was tested by the analysis of solutions containing varying amounts of antimony, which were unknown to the analyst. See Table, p. 26.

We do not claim for the method a greater accuracy than within ten per cent.

#### THE DELICACY OF THE METHOD.

Amounts of antimony as small as five micromilligrams are readily recognized by use of the 4 mm. strip. Less than this quantity may be

<sup>4</sup> See Table II, Sanger and Black<sup>1</sup>.

<sup>5</sup> These Proceedings, **42**, 719 (1907); Jour. Soc. Chem. Ind., **26**, 585 (1907); Zeitschr. f. anorg. Chem., **55**, 205 (1907).



TABLE.

No. of Analysis.	Sb <sub>2</sub> O <sub>3</sub> taken. Tartar Emetic Solution.	Total Weight Diluted Solution.	Wt. Diluted Solution taken for Analysis.	Reading of Band.	Sb <sub>2</sub> O <sub>3</sub> Found.	Sb <sub>2</sub> O <sub>3</sub> Found. Mean.	Per Cent Sb <sub>2</sub> O <sub>3</sub> Found.
4	mg. 0.06	gm. 25.15	gm. 4.67 8.62 10.63	mmg. 8 15 25	mg. 0.043 0.044 0.059	0.049	82
2	0.12	25.92	4.31 2.61 7.11	20 10 35	0.120 0.099 0.128	0.116	97
6	0.20	23.04	2.59 1.72 4.23	25 17 40	0.222 0.228 0.218	0.223	112
2, a	0.25	26.07	5.18 3.43 1.05	45 35 10	0.227 0.266 0.248	0.247	99
9	0.60	21.63	0.79 0.97 1.09	22 26 32	0.602 0.580 0.635	0.606	101
8	1.20	23.74	0.81 0.84	35 35	1.03 0.99	1.01	84
8, a	1.50	24.30	0.46 0.61 0.59	30 40 40	1.58 1.59 1.65	1.61	107
7	1.60	21.32	0.39 0.27 0.53	35 20 45	1.91 1.58 1.81	1.77	111
4, a	2.50	27.76	0.44 0.44 0.44	45 40 45	2.84 2.52 2.84	2.73	109
3, a	3.00	29.99	0.56 0.56 0.54	50 60 60	2.68 3.21 3.33	3.07	102
Average Percentage . . . . .							100

indicated, but the estimation is difficult. By using smaller strips, however, a more accurate reading of the band may be obtained and the delicacy of the method increased. These small strips, as in the arsenic method, are made by cutting the large strip in two and again dividing



these pieces lengthwise, giving a piece 2 mm. wide and 35 mm. long. This is inserted in a tube of 2 mm. diameter, affixed to the usual deposition tube by a rubber connector. A series of standards is then made of any amounts of the smaller quantities of which it may be desirable to get an approximate estimate. The upper part of the Plate shows the bands obtained from amounts of antimony equivalent to 0.5, 0.8, 1.0, 2.0, 5.0, and 10.0 mmg. of antimonious oxide.

The bands obtained from 0.5 and 0.8 mmg. are perfectly distinct, but not always differentiated with clearness. From amounts below 0.5 mmg. we have not been able to obtain any indication on the 2 mm. strip. It is safe, therefore, to set the practical limit of the delicacy of the method at 1 mmg. (0.001 mg.) of antimonious oxide (0.0008 mg. of antimony). The absolute delicacy, however, is very nearly half of this amount, — 0.0005 mg. of antimonious oxide, which is equivalent to 0.0004 mg., or one twenty-five-hundredth of a milligram of antimony.

Sanger and Gibson<sup>5</sup> were able to detect and identify by the Berzelius-Marsh method 0.005 mg. of antimonious oxide, but the deposit in the tube from 0.001 mg. was faint. It will thus be seen that the "band" method is much more delicate than the "mirror" method. It is also more convenient and accurate, for the bands are subject to no irregularity of formation comparable to the difficulty of obtaining a mirror of metallic antimony entirely free from oxide. The mirror method, however, is still of value as a confirmation of the other and a check upon its results. The two methods can be applied, if desired, to different portions of the solution which has been prepared for analysis.

The application of the method to the analysis of products containing antimony is under consideration in this laboratory, but we have contented ourselves for the present with showing that very small amounts of antimony may be estimated by it in a solution properly prepared for analysis. A study of its application should include the separation of small amounts of arsenic or antimony from relatively large amounts of the other, concerning which we have now no reliable information.

